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UNITED STATES DEPARTMENT OF AGRICULTURE

BULLETIN No. 620

Contribution from the Forest Service
HENRY S. GRAVES, Forester

Washington, D. C. PROFESSIONAL PAPER March 14, 1918

# EFFECT OF VARYING CERTAIN COOKING CONDITIONS IN THE PRODUCTION OF SULPHITE PULP FROM SPRUCE

By

S. E. LUNAK, Chemist in Forest Products

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### PURPOSE OF THE EXPERIMENTS.

Forest products investigations of the Forest Service include the study of problems connected with the manufacture of pulp and paper from wood, so as to utilize waste material from the lumber and other industries wherever possible, to increase the efficiency of present methods of making pulp, and to determine the practicability of making pulp from woods hitherto little used or considered unfit. Bulletins have been issued on the soda, sulphate, and ground-wood processes showing the effect which the different fundamental variables have on the resultant pulp. This bulletin supplies similar information for the sulphite process, and shows what effect the amount of combined sulphur dioxide ($SO_2$), the total sulphur dioxide, and the temperature have upon the color of the paper, the duration of the cooking period, the yield of pulp and screenings, and the consumption of bleach.

The original patent for the making of sulphite pulp states that it can be produced with or without the addition of a base to the cooking liquor but that a lighter product can be obtained when a

NOTE.—Acknowledgement is made to Mr. O. L. E. Weber, formerly of the Forest Products Laboratory, and Dr. Otto Kress, in charge of the section of pulp and paper, Forest Products Laboratory, for many valuable suggestions and much helpful advice.

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base is present. Lime is the base in most common use. For a long time it was not known how much of this was necessary to make good pulp, most mills simply taking the acid that their systems gave them. Many are still following that practice. Most mills have a good idea of how the different factors affect their cooking, but there is no published report on the subject. It was to furnish detailed information on just how much each of the various factors influences the cooking and to supply a basis for future experimental work that this investigation was undertaken.

## THE SULPHITE PROCESS.

The inventor of the sulphite process, Benjamin C. Tilghman, of Philadelphia, took out a patent in the year 1867, in which he describes a method of boiling under pressure wood or other vegetable material in a solution containing sulphurous acid, with or without the addition of sulphites, until a fibrous product is obtained suitable for the manufacture of paper. The foundation of the sulphite pulp industry rests upon these patents; yet Tilghman had to abandon his process because his financial backers withdrew their support upon finding out that sulphurous acid corrodes iron and that the inventor was having difficulty in obtaining a suitable lining for his digester when he tried to work his process on a large scale.

For some time this difficulty hindered the development of the process. In 1886 cement and special brick linings were introduced in some mills and gave such good satisfaction from the start that it was not long before they were universally adopted. The solution of this problem insured the commercial success of the sulphite industry, and from this time on it has had a rapid growth, until now it is the most important pulp making process in the United States, as is shown by the figures in Table 1 taken from the census reports.

TABLE 1.—*Quantity of wood pulp produced in the United States.*

| Process. | 1890 | 1899 | 1909 | Value (1909). | 1916 | Value (1916). |
|---|---|---|---|---|---|---|
| | *Tons.* | *Tons.* | *Tons.* | | *Tons.* | |
| Sulphite | 59,686 | 417,646 | 1,027,012 | $44,600,000 | 1,306,217 | $60,702,459 |
| Soda | 87,853 | 172,142 | 287,945 | 12,770,000 | 183,106 | 8,251,219 |
| Ground wood | 290,158 | 568,284 | 1,201,832 | 25,200,000 | 1,505,547 | 32,547,704 |

## KINDS OF WOOD USED.

In the early days spruce was almost the only wood used in making sulphite pulp, but it was not long before hemlock and balsam began to be used extensively. At the present time some mills are cooking tamarack and poplar, and on the west coast white, red, amabilis, and grand fir, sitka and Engelmann spruce, western hemlock, and other woods are finding favor. No doubt it will not be long before

many other woods will be used, as spruce is becoming too expensive. The sulphite process can not be used on woods that contain much pitch, because a large part of the pitch remains in the pulp and later causes much trouble on the wires of the paper machine. This problem has been the subject of much study and investigation but no successful method has yet been found for cooking such wood by this process and eliminating the resin.

The curves in figure 1 show the per cent of the principal woods used in the sulphite process from the year 1900 to 1911. The consumption of spruce is decreasing, and other woods are being used more

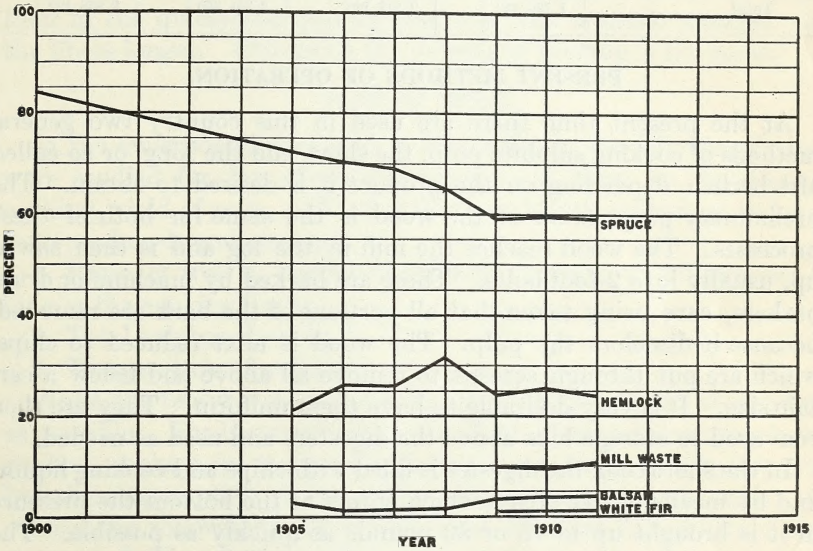



FIG. 1.—Consumption of wood by the sulphite process in the United States, 1900–1911.

extensively than before. Table 2 gives in detail the kind and amount of each wood used.

TABLE 2.—*Consumption of wood by the sulphite process in the United States.*

[From Census and Forest Service Reports.]

| Kind of wood. | 1900 | | 1905 | | 1906 | | 1907 | |
|---|---|---|---|---|---|---|---|---|
| | Cords. | Per cent. | Cords. | Per cent. | Cords. | Per cent. | Cords. | Per cent. |
| Spruce | 790,153 | 83.9 | 1,176,930 | 72.2 | 1,374,212 | 70.2 | 1,422,400 | 69.1 |
| Hemlock | ..... | ..... | 344,579 | 21.1 | 516,512 | 26.4 | 541,113 | 26.2 |
| Poplar | ..... | ..... | ..... | ..... | ..... | ..... | 1,536 | .1 |
| Balsam | ..... | ..... | 45,943 | 2.8 | 22,314 | 1.1 | 28,356 | 1.4 |
| Pine | ..... | ..... | 18,606 | 1.1 | 3,600 | .2 | 3,200 | .2 |
| White fir | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... |
| Slab wood and other mill waste | ..... | ..... | ..... | ..... | ..... | ..... | ..... | ..... |
| All other species | 152,364 | 16.1 | 44,341 | 2.8 | 41,981 | 2.1 | 62,890 | 3.0 |
| Total | 942,517 | ..... | 1,630,393 | ..... | 1,958,619 | ..... | 2.059.495 | ..... |

TABLE 2.—*Consumption of wood by the sulphite process in the United States*—Continued.

| Kind of wood. | 1908 | | 1910 | | 1911 | | 1916 | |
|---|---|---|---|---|---|---|---|---|
| | Cords. | Per cent. | Cords. | Per cent. | Cords. | Per cent. | Cords. | Per cent. |
| Spruce | 1,131,377 | 65.2 | 1,332,153 | 59.5 | 1,391,047 | 59.2 | 1,803,217 | 63.1 |
| Hemlock | 544,131 | 31.4 | 574,109 | 25.6 | 563,535 | 24.0 | 647,738 | 22.7 |
| Poplar | 3,734 | .2 | 625 | ..... | 4,101 | .2 | 2,991 | .1 |
| Balsam | 24,761 | 1.4 | 81,932 | 3.7 | 100,339 | 4.2 | 213,569 | 7.5 |
| Pine | 3,484 | .2 | 4,720 | .2 | 4,286 | .2 | 8,209 | .3 |
| White fir | ..... | ..... | 27,797 | 1.2 | 32,498 | 1.4 | 35,865 | 1.3 |
| Slab wood and other mill waste | ..... | ..... | 219,519 | 9.7 | 254,914 | 10.8 | 140,758 | 4.9 |
| All other species | 28,772 | 1.6 | 1,285 | .1 | 830 | ..... | 3,775 | .1 |
| Total | 1,736,259 | ..... | 2,242,140 | ..... | 2,351,550 | ..... | 2,856,122 | ..... |

## PRESENT METHODS OF OPERATION.

At the present time there are used in this country two general methods of cooking sulphite pulp, the short and the long, or so-called Mitcherlich, depending on the product it is desired to obtain. The preliminary preparation of the wood is the same for both of these processes. The wood reaches the mill in the log and is then sawed up, usually into 2-foot bolts. These are barked by machine or drum barkers, care being taken that all portions of the bark are removed, because it discolors the pulp. The wood is next reduced to chips, which are put through screens to remove all above and below a certain size. It is very desirable to have them uniform. They are then conveyed to storage bins above the digesters and used as needed.

In the short cook the digester is filled with chips and cooking liquor, and by means of live steam which enters at the bottom the pressure in it is brought up to 75 or 80 pounds as quickly as possible. The pressure is then kept at this point and the temperature is gradually raised, so that a temperature of 154° C. is reached at the end of about 7 to 9 hours. While the temperature is being raised, the $SO_2$ gas which is being driven from the liquor in the digester is constantly relieved and reclaimed by absorption directly in tanks or in towers filled with stone. The pressure in the digester is due partly to the steam present and partly to the gas liberated. As the cook progresses the steam pressure increases, but the gas pressure decreases until at the end of the cook there are only a few pounds of pressure due to the $SO_2$ gas present. The pressure in the digester is kept the same by means of an automatic arrangement, which lets in more steam when the digester is being relieved and shuts it off again when the relief valve is closed. At the end of 3 or 4 hours the condensation in the digester causes it to fill up with liquor, which is relieved usually through an opening about 3 feet from the top. Toward the end of the cook the liquor in the digester gets darker and darker until it reaches a light coffee color. The end point is determined by the color

and smell of the liquor, and how accurately it is attained depends in most mills wholly on the experience and judgment of the man in charge of the cook. When the cook is finished, a large valve is opened at the bottom of the digester and the contents blown through a pipe into a blow pit, where they are thoroughly washed.

In the slow cook process the digester is heated by lead coils placed in the bottom. Because of the caking of calcium monosulphite on them, however, these are rapidly going out of use and the heating is being done by direct steam. A somewhat weaker acid is used than for the short cook, and the pressure is held at from 60 to 65 pounds. A cook lasts from 20 to 30 hours, but the digesters are much larger than in the quick-cook process and the pulp is much stronger and the fibers longer. Otherwise the process of cooking is the same.

## PLAN OF TESTS.

In the experiments recorded in this bulletin, the following factors were studied for the effect of variations in them on duration of cooking, yield of pulp, yield of screenings, bleach consumed, color of pulp produced, and strength.

1. Ratio of free to combined sulphur dioxide, or the amount of lime in the cooking liquor.
2. Total sulphur dioxide.
3. Temperature of cooking.

While one factor was studied the other two were kept as constant as possible. For instance, when the effect of temperature was being studied, cooks were made with definite variations in temperatures, but the consumption of the cooking liquor remained the same. Of course, the following factors were kept constant for all the cooks: Amount of chips, 74.2 pounds bone dry; moisture condition of chips, air dry; amount of acid, 63 gallons; time to reach 100° C., 2 hours; time to reach maximum temperature, 3 hours.

## APPARATUS.

A plan of the apparatus used in cooking is shown in figure 2. The digester was lined with a half and half mixture of special cement and quartz sand. This lining was about 1½ inches thick, and on top of it was put a layer of pure cement 1 inch thick.

The equipment used for making the pulp into paper consisted of a pulp shredder, 15-pound Emerson beater, 6-plate diaphragm screen with 0.009-inch slots, and a 15-inch Fourdrinier paper machine. A 50-pound Marx beater was used on the last six cooks.

The wood used in these experiments was white spruce (*Picea canadensis*) cut in the State of Wisconsin. This wood was cut into five-eighths-inch chips in a small chipper of the usual design and the chips screened, after which they were ready for the digester.

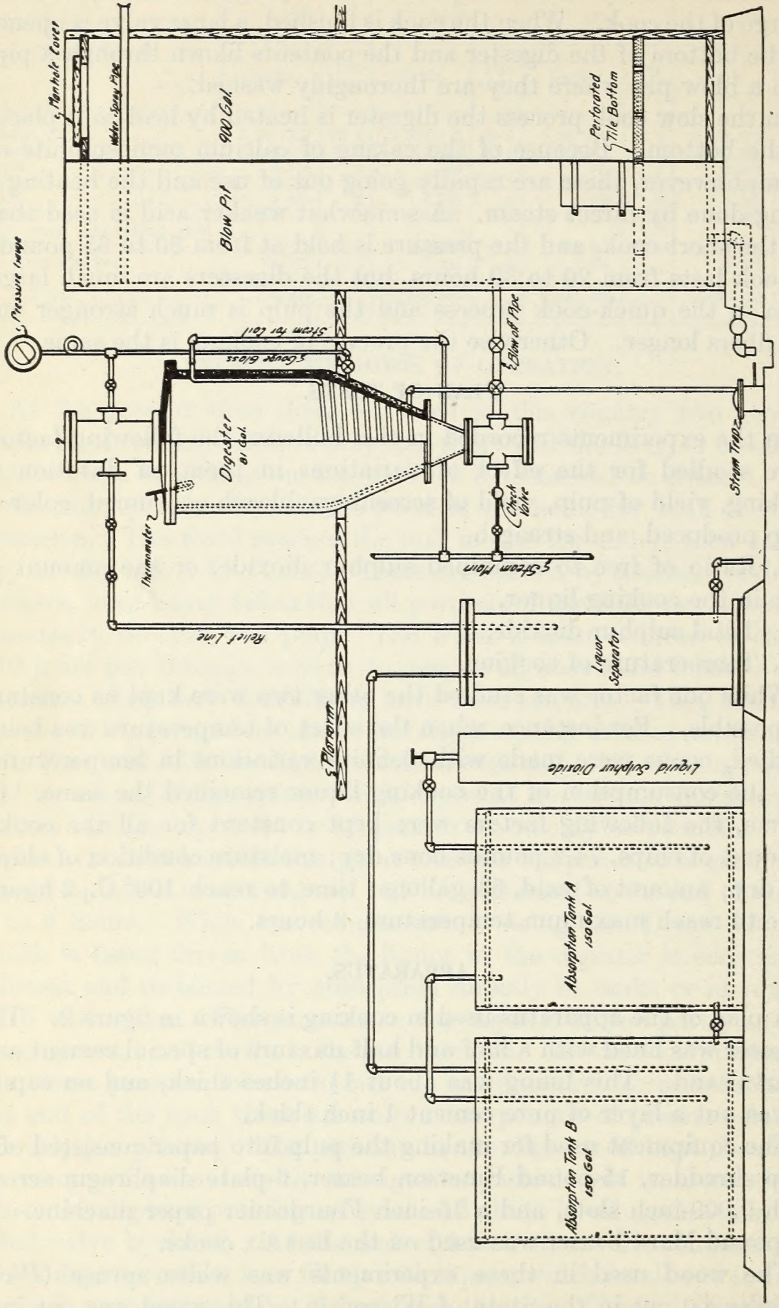



FIG. 2.—Plan of apparatus used in cooking.

## METHOD OF CONDUCTING EXPERIMENTS.

### LIQUOR MAKING.

The sulphur dioxide used in making the liquor in these experiments was obtained in liquid form under pressure in iron cylinders 5 feet 5 inches in height and 11 inches in diameter, each cylinder holding about 200 pounds. By obtaining the sulphur dioxide in this way the cooking liquor can be made to any desired strength in a couple of hours by simply turning a valve, which is an ideal way of handling the gas for experimental work.

In making the cooking liquor for the first cook the gas from one of these cylinders was passed to the bottom of an absorption tank, containing the desired amount of milk of lime, by means of a lead pipe which contained a number of small openings in the end. The procedure in making the subsequent liquors was as follows: When a cook was finished, the pressure in the digester was blown down to about 65 or 70 pounds, and the gas thus liberated was passed through a separator, which removed the liquor, to the bottom of the absorption tank B (fig. 2) which contained a dilute solution of milk of lime. The liquor from tank B (fig. 2) was then pumped to the make-up tank A (fig. 2) and, if necessary, water was added so that it contained at least 80 gallons. Sulphur dioxide gas was then passed into this tank from the cylinder and the liquor in the tank analyzed (for methods of analysis see p. —) every half hour. The rate at which the gas was being absorbed could then be calculated and the time in which the desired strength would be obtained could be determined very closely. The cylinder could also be put on a scale and the desired amount of gas calculated and the weight obtained by difference. After the tank B (fig. 2) was emptied it was again filled with a dilute solution of milk of lime [1] and any gas that was not absorbed in the make-up tank passed through a lead pipe back into this tank. Very little gas would be given off, however, it being absorbed almost up to the full pressure of the cylinder. While the gas is being absorbed in the make-up tank, milk of lime can be added as desired or cooking liquor can be made containing no lime at all. When the liquor is of the desired strength it is ready to be pumped to the digester to start the next cook.

While these experiments were in progress it became impossible to secure a supply of liquid sulphur dioxide, and in order to continue it became necessary to make the gas. A description of some of the methods tried may be of assistance to anyone contemplating doing experimental work along this line.

---

[1] The lime used in the experiments had the following analysis:

| | | | |
|---|---|---|---|
| $SiO_2$ | 0.56 | MgO | 32.31 |
| $Fe_2O_3$&$Al_2O_3$ | 1.20 | $CO_2$&$H_2O$ | 1.90 |
| CaO | 64.19 | | |

The first method tried was the ordinary one of burning sulphur and passing the gas through a milk of lime solution. A small sulphur stove, with a flat bottom and a burning area of about 3 square feet, was designed. The gas, after leaving the stove, passed through a cooling system and through three absorption tanks of about 150 gallons capacity, so arranged that it entered the bottom of the first tank, the unabsorbed portion then passed to the bottom of the next tank, and so on to the third one, the gas being moved by suction. The two tanks nearest the stove contained water alone and the last one milk of lime. After the system had been going for about three hours, samples were taken from each tank and analyzed. The liquor in each of the first two tanks contained about 1.20 per cent of $SO_2$ and in the last tank 3.10 per cent, all of it calcium bisulphite; nor could the solutions be made any stronger by continuing the operation, the gas simply passing through without being absorbed. The reason that the solutions would not become stronger is that the solubility of $SO_2$ gas depends on its dilution. Pure $SO_2$ gas is very soluble in water, it being possible to make solutions containing as high as 10 per cent; but just as soon as it is diluted with some other gas that is not soluble in water, such as nitrogen, the strength of the solutions becomes much less. Thus, the gas produced here contained about 17 per cent $SO_2$ and would produce only a certain strength of solution no matter how long the gas was passed through; the solutions became even weaker if the fire in the burner got low. As solutions had to be made to meet a wide range of concentrations, this method was abandoned.

It was then decided to absorb the gas in two towers, 15 feet in height and 15 inches in diameter, made of sewer crock, and filled with broken tile, to see how strong a solution could be obtained by absorbing the gas in pure water alone. The gas from the burner entered the first tower at the bottom and met water trickling down through the broken tile, left it at the top, and passed into the bottom of the next tower. The strongest acid in the first tower contained 2.20 per cent $SO_2$ and the second 1.10 per cent. As this acid was not strong enough, it was decided to pump the acid from the towers into the digesters, there drive off the gas by heat and reabsorb it in one of the tanks. While acid by this method could be brought to any desired strength, it took so much time and attention that it was not practical.

The next method tried was to secure the action of sulphuric acid upon sodium bisulphite according to the equation $2NaHSO_3 + H_2SO_4 = Na_2SO_4 + 2SO_2 + 2H_2O$. For this purpose, a 16-inch pipe, 4 feet long, was flanged at both ends and lead-lined. The desired amount of sodium bisulphite mixed with water was fed in through an opening in the upper flange, which was then closed. The sulphuric acid was

fed in through a U-tube, the receiving end (which was about 5 feet higher than the top of the cylinder) having a large lead dish attached, into which the sulphuric acid was poured. As the sulphuric acid mixed with the sodium bisulphite, pure sulphur dioxide was liberated. This was passed through a Woulf bottle, containing a little water as a trap to catch any sulphuric acid which might boil over. From here the gas entered the absorption tank. As the gas produced was pure, sulphur dioxide solutions of any strength desired could be produced.

Making the cooking liquor was not so quick or easy, nor was it so simple and convenient with the gas as with the sulphur dioxide in liquid form, so that the liquid was again used as soon as a supply was once more available.

### METHOD OF COOKING.

The method of cooking received a great deal of consideration, as one variable, the pressure, was hard to control. The ordinary method of cooking by direct steam and relieving sulphur dioxide at the top is unsuitable for experimental cooking because, first, direct heating causes too much condensation of steam in the digester with consequent dilution of the cooking liquor and, second, relieving $SO_2$ at the top would have a tendency to destroy the effect which we were trying to study. For example, in studying different strengths of cooking liquor, there would be no object in starting with a strong liquor, only to blow all the sulphur dioxide out of the digester in a short while. Therefore it was decided to heat the digester by means of indirect steam, that is, by means of a lead coil placed in the bottom of the digester; and no gas was allowed to escape until the cook was finished. While this method of cooking differs from that used in commercial practice, it will bring out more than any other the factors under investigation.

The method of procedure in making a cook was as follows: The chips, the amount of which had previously been determined by means of a bone-dry sample, and which remained the same for every cook, were put into the digester and 63 gallons of cooking liquor in each case were then run in and the digester tightly closed. The steam to the coil was then turned on and the cook started. The cooking curve for temperature was the same in each case, taking two hours to reach 100° C., and three hours to reach the maximum temperature, where it was held until it was finished, the pressure being allowed to go where it would. Keeping the full strength of the liquor to the finishing point in this way gave a hard pulp, which had the characteristics resulting from beating for a long time.

The curves for all cooks are shown in figures 3 to 7. In each figure, curve 1 shows the way the temperature was increased and

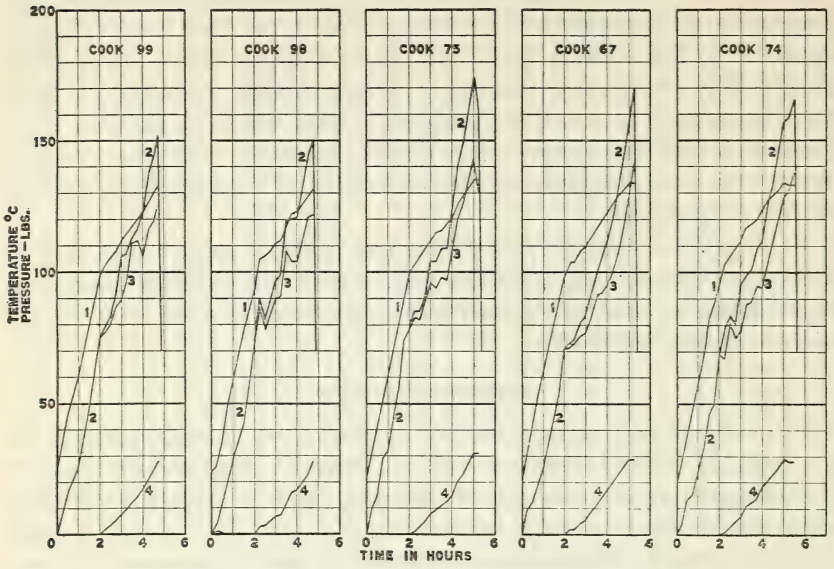



FIG. 3.—Cooking curves for cooks 99, 98, 73, 67, and 74. 1, temperature; 2, gauge pressure; 3, gas pressure; 4, steam pressure.

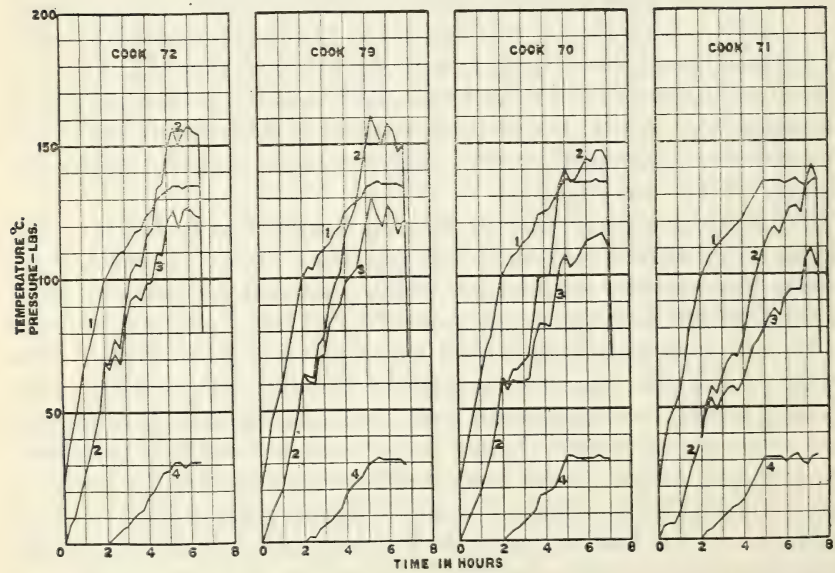



FIG. 4.—Cooking curves for cooks 72, 79, 70, and 71. 1, temperature; 2, gauge pressure; 3, gas pressure; 4, steam pressure.

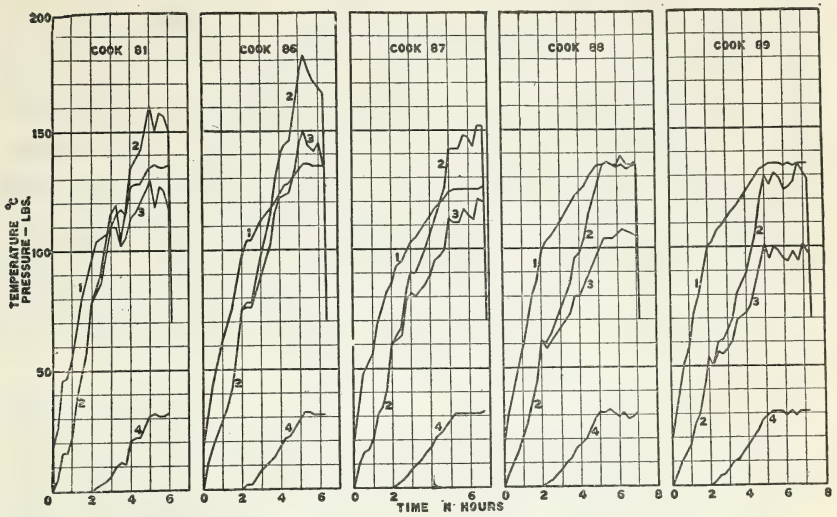



FIG. 5.—Cooking curves for cooks 81, 86, 87, 88, and 89. 1, temperature; 2, gauge pressure; 3, gas pressure; 4, steam pressure.

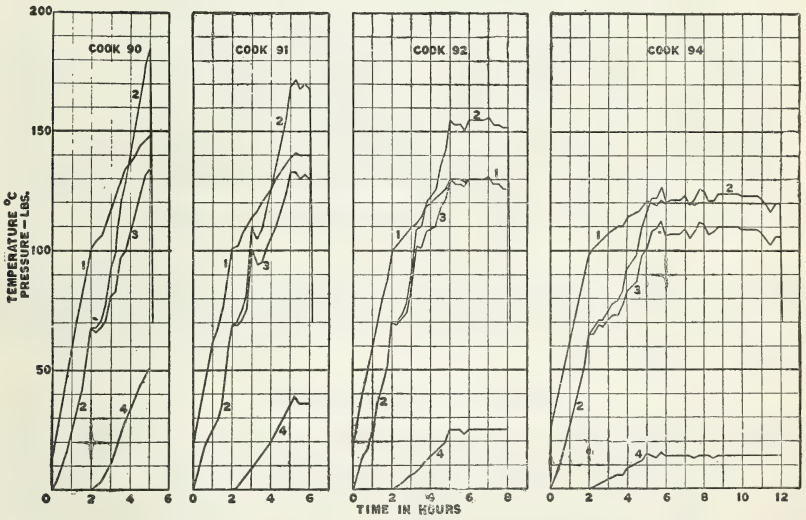



FIG. 6.—Cooking curves for cooks 90, 91, 92, and 94. 1, temperature; 2, gauge pressure; 3, gas pressure; 4, steam pressure.

curve 4 shows the steam pressures corresponding to the temperatures. Curve 2 shows the gauge pressure, and curve 3 shows the gas pressure, which is the difference between the gauge pressure and the steam pressure at any given point. Endeavor was made to keep the temperature curve a straight line, but sometimes the temperature would drop and then to reach the desired temperature the observer would turn on full pressure of steam, which caused a rapid increase in the gauge pressure and accounts for some of the bulges in the gas and gauge pressure curves. Every 15 minutes readings were taken of the temperature and pressure. Owing to the peculiar type of construction of the digesters and the position of the thermometer well, it was necessary at the end of about two and one-half hours of cooking to inject steam into the digester to make up for the liquor taken up by

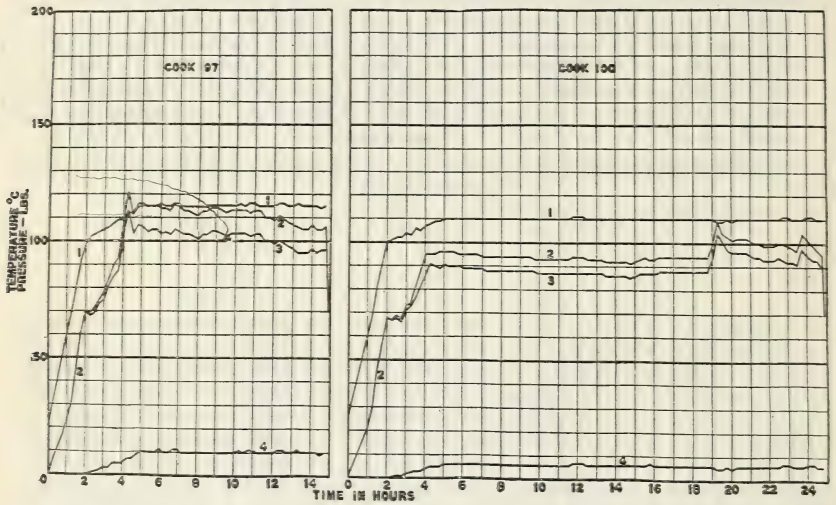



FIG. 7.—Cooking curves for cooks 97 and 100. 1, temperature; 2, gauge pressure; 3, gas pressure; 4, steam pressure.

the chips, or the liquor level would sink below the thermometer well and not give the correct reading. This was done as uniformly as possible for every cook.

### METHOD OF FINISHING COOK.

With the composition of liquor and temperature changing each time, a great deal of difficulty was experienced at first in knowing when to finish cooks so that each one would be pulped to the same degree. The digester was equipped so that cold liquor for sampling could be obtained by passing it through a condenser.

An attempt to finish cooks to the same sulphur dioxide content was made, but some would be overcooked while others would be almost raw, as a result of using liquor containing different amounts of $SO_2$. This method can only be used when the same kind of liquor

is used for every cook. What is ordinarily known as the lime test was also tried. In this test some of the cooking liquor from the digester was put in a test tube containing a slight excess of ammonia, and if the lime came down in a dark floculent condition it was time to blow the cook. While this method gave promise, the results obtained with it were very erratic and it was finally abandoned. An attempt to judge the degree to which the chips in the digester had been cooked by blowing some out into a canvas bag and shaking in a cylinder was also unsuccessful because of the great irregularity in the samples. Sometimes a sample would show more uncooked shives than the one taken half an hour before. Judging the condition of the stock by dyeing with a basic color, such as diamond green, also showed no regularity. Nor did the depth to which a 13 per cent solution of nitric acid would color the pulp indicate the end point accurately.

It is common practice in pulp mills to judge when a cook is finished by the color, smell, and analysis of the liquor; but with the wide variety of conditions under which the cooks in this study were made it was at first thought that these methods would not be applicable. However, it was decided to give the color method a trial. The liquor in the digester near the end of the cook has a light caramel color which darkens rapidly on standing.

To finish a series of cooks to the same degree of cooking it is necessary to have some fixed color as a standard for comparison. Most solutions of organic dyes change in color rapidly when exposed to the light and no combination of mineral dyes could be made that would match the color wanted close enough. The color desired strongly resembles the color of coffee extract, and it was decided to see if this could not be made permanent enough to run a series of cooks. Two solutions, which had been clarified with the white of an egg, were made, one light and one dark, and the shade desired was matched up as closely as possible by mixing the two. Formaldehyde solution was then added to stop fermentation and no change in color of the coffee extract was perceptible, even after it had been in use for several months. The results obtained by using this standard were satisfactory from the first. All that is necessary to duplicate a certain cook is to match the color of the liquor at time of finishing with coffee extract to be used as a standard. This ought to find application commercially, as the man in charge will not have to depend on his memory when he wishes to duplicate a certain cook. During the progress of the cook, samples of the liqour were withdrawn from time to time in a test tube and the color compared with the standard. When the color matched, the steam to the coil was turned off, the pressure in the digester relieved to 70 pounds in five minutes, and the cook blown into the blow pit.

### METHOD OF HANDLING PULP.

The blow pit was fitted up with a false bottom made of perforated tile. The pulp was washed five or six times with water and allowed to drain each time. When it had been sufficiently washed, it was shoveled out into a canvas bag, placed in a perforated iron cylinder, and then pressed in a 70-ton knuckle joint power press until it was about 30 per cent dry. It was then shredded, so that the bone-dry weight determination could be made accurately, weighed, and sampled for moisture determination. The pressing operation caused the pulp to ball or stick together, so that it had to be opened up in the beater before it could be screened. This was done with the roll well up, after which it was pumped to a stock tank and diluted with water. From here it ran upon a six-plate diaphragm screen with slots 0.009 of an inch in width. After being screened it ran through a stock thickener, where most of the water was removed. The screenings were carefully collected, pressed, weighed, and sampled for moisture determination. Some of the screened pulp was saved for bleach and other determinations, after which it was put into a 15-pound Emerson beater, mixed with water and beaten, with the roll off the bed plate, for one-half hour. The stock was then run into paper over a 15-inch Fourdrinier machine and samples of the uncalendered sheets taken for strength tests.

The methods of making the bleach, yield, and strength determinations are given on page 22.

### EFFECT OF VARYING THE RATIO OF FREE TO COMBINED $SO_2$ OR THE AMOUNT OF LIME IN THE COOKING LIQUOR.

In order to determine the effect of varying the ratio of free to combined $SO_2$, cooks were made using a liquor with a total sulphur dioxide content of 5 per cent and a maximum temperature of cooking of 135° C., the amount of $SO_2$ combined with lime being varied from 0.30 to 2.09 per cent. The curves in figure 8 show how variations in the combined $SO_2$ affected the color rating, duration of cook, yield of screened and unscreened pulp, yield of screenings, and bleach consumption.

A decrease in the combined $SO_2$, other conditions being constant, has a tendency to shorten the duration of the cooking time. Increasing the amount of combined $SO_2$ to 1 per cent has a tendency to make the pulp lighter, but the color remains constant when the combined $SO_2$ is increased over 1 per cent. The color determinations for the machine-made sheets were made by means of a tint photometer (p. 22). The higher the parts black, the darker the sheet.

The yield of screenings and unscreened pulp remains constant when the combined $SO_2$ is decreased to 1 per cent, but any decrease below this shows a sharp increase in both of these factors. The

yield of screened pulp increases as the combined $SO_2$ is increased to 1 per cent, but beyond this remains constant. The amount of bleaching powder necessary to bring the pulp to a standard white decreases as the combined $SO_2$ is increased to about 1 per cent, but

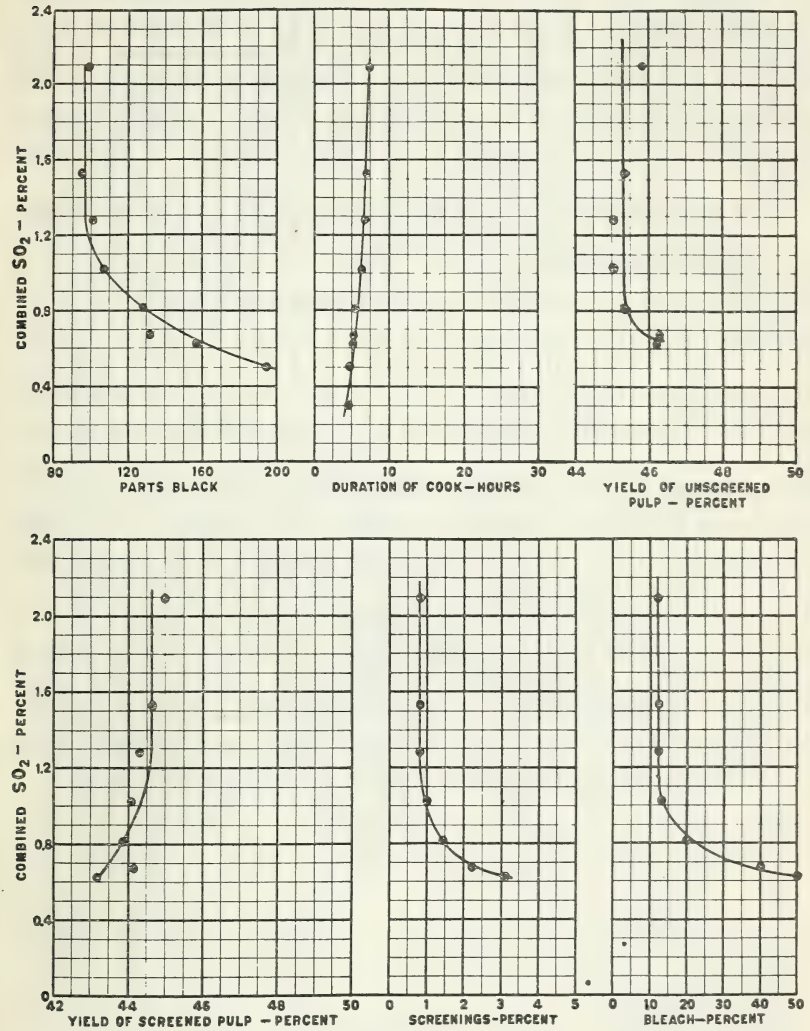



FIG. 8.—Effect of varying the amount of combined $SO_2$ in the cooking liquor.

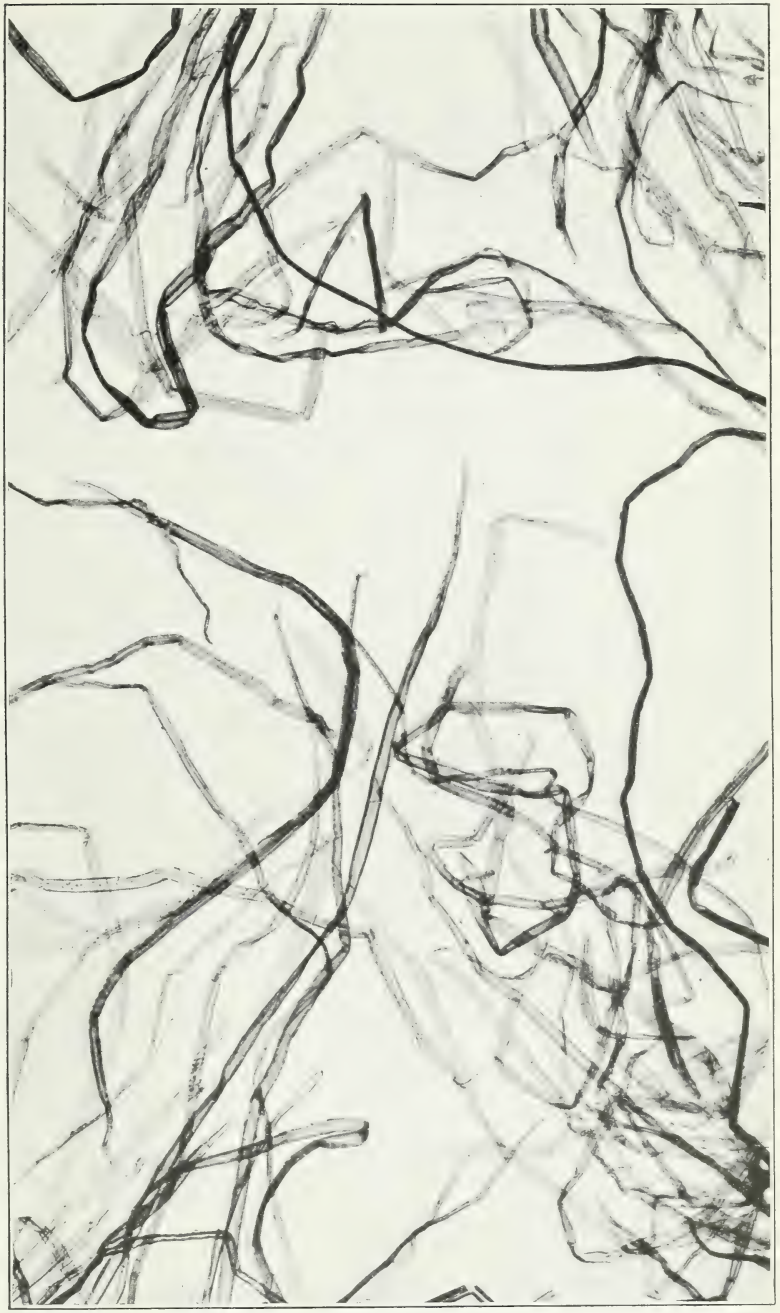
any increase beyond this point does not produce any further change in color.

The amount of combined $SO_2$ does not seem to have much influence on the different factors studied, provided it is over 1 per cent, but any decrease below this caused marked changes in the character and

yield of pulp. One cook was made where the cooking liquor contained only 0.30 per cent of combined $SO_2$, and the result was that the chips came out of the digester looking as if they had received only a steaming treatment. They were softened, but black, and gave a yield of 60.40 per cent, showing that the wood had not been thoroughly cooked. When the combined $SO_2$ is decreased too much, there is a darkening of the liquor without the corresponding cooking action, causing a browning of the pulp. Apparently a certain amount of lime must be present in the cooking liquor to get complete pulping, but its effect becomes less as it is increased beyond 1 per cent combined $SO_2$.

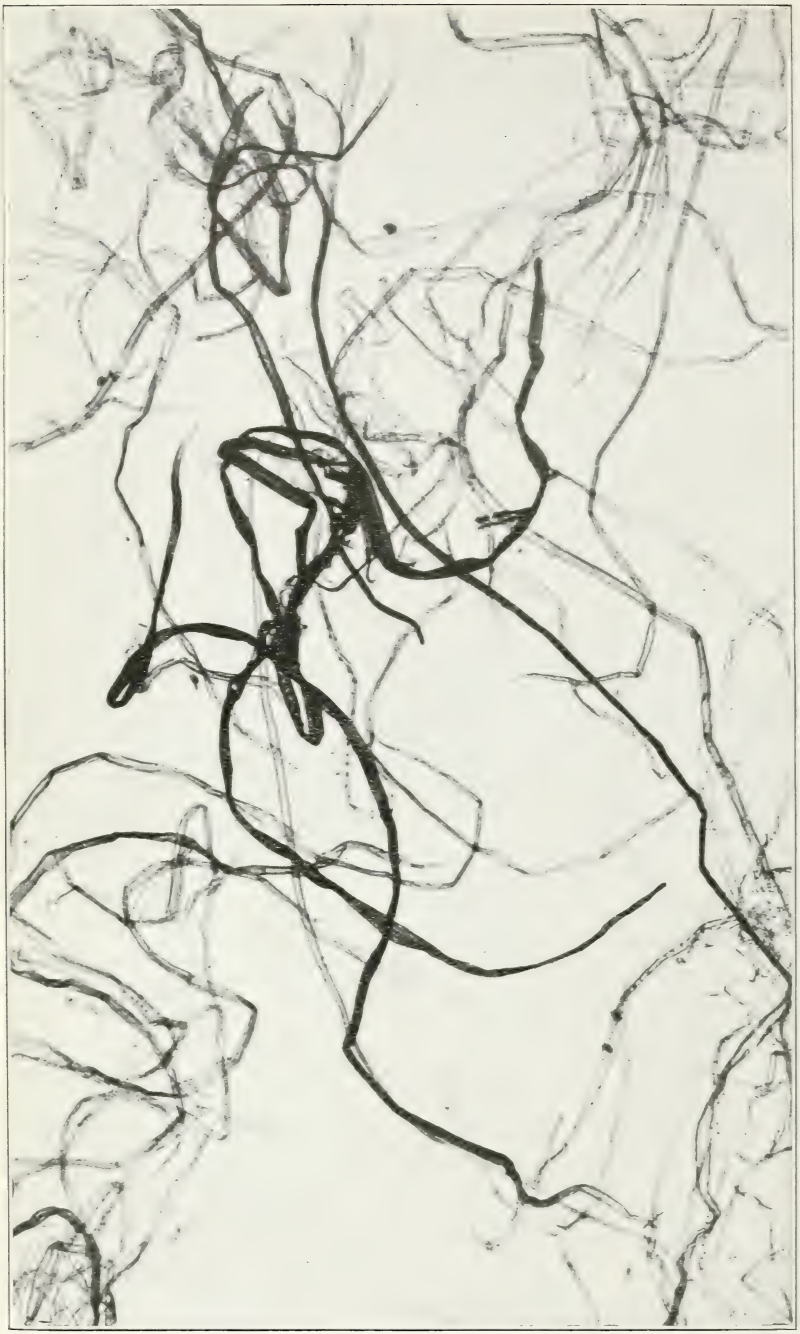
At the present time, the only method of giving a numerical value to the strength of the fibers of a pulp is to make strength tests of paper produced from that pulp. In order to obtain any regularity of results in strength of paper in a series of tests it is necessary that the beating of the pulp, formation of the sheet, heat in the driers, humidity at which the strength tests are made, and probably other factors must remain constant. Most of these, then, depend on the personal equation of the machine tender, and where some of the runs may be made a week apart, conditions are likely to vary. This probably explains the irregularity of the strength results as given in Table 3. If they show anything at all, it is that above 0.80 per cent the amount of combined $SO_2$ has no influence on the strength of the paper produced but below that there is a tendency to decrease in strength.

Photomicrographs of the pulps secured in cooks 75, 74, 72, and 71 are shown in Plates I, II, III, and IV. It will be noted that there is a gradual change in the appearance of the fibers. Cook 75 was made with liquor containing 0.62 per cent of combined $SO_2$, and cook 71 with 2.09 per cent. The former contains much lignified fiber, while the latter seems to be thoroughly cooked.

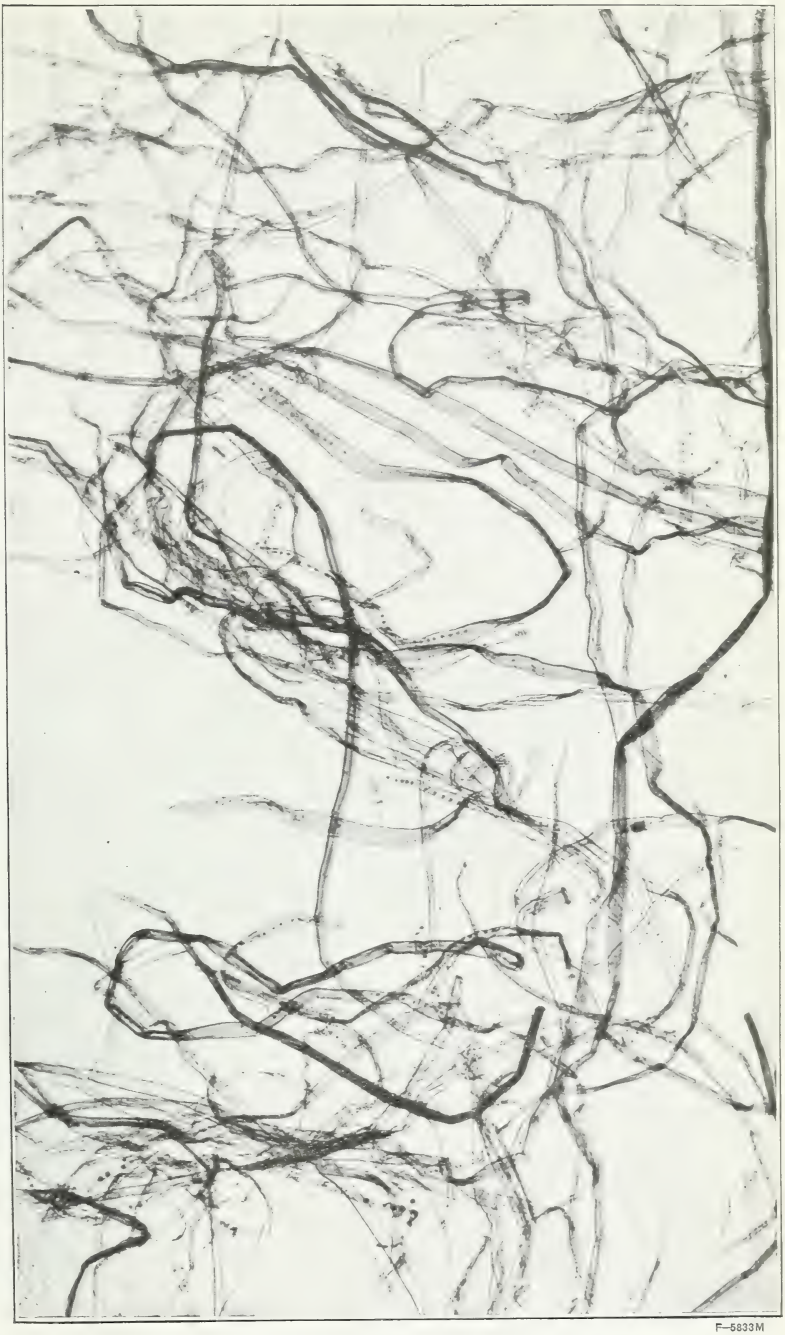


F-5834M

PULP PRODUCED IN COOK 75.

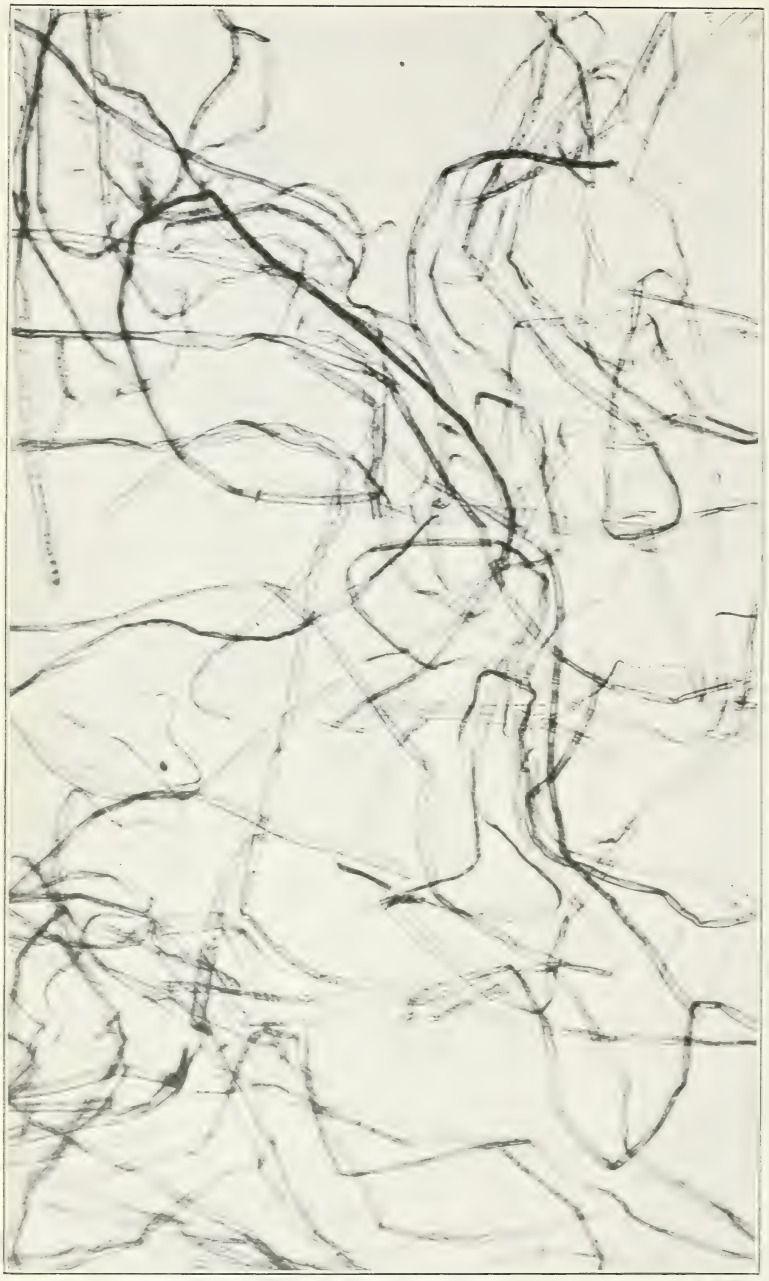



PULP PRODUCED IN COOK 74.



F—5833M

PULP PRODUCED IN COOK 72.



F—5540M

PULP PRODUCED IN COOK 71.

TABLE 3.—*Cooking conditions and results.*

VARYING AMOUNT OF COMBINED $SO_2$.

| Cook No. | Maximum temperature. | Time to reach 100° C. | Time to reach maximum temperature. | Bone-dry chips used. | Gallons acid. | Total $SO_2$. | Free $SO_2$. | Combined $SO_2$. | Ratio F/C. | Duration of cook. | Yields—bone-dry basis. | | | Bleach consumption. | Tintometer readings. | | | | Strength tests. | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | Yield of unscreened pulp. | Screenings. | Yield of screened pulp. | | Red. | Green. | Blue. | Black. | Weight per ream | Mullen test. | Strength ratio per pound. | Strength factor per 0.001-inch thickness. | Breaking length average. | Stretch average. | Folds average. |
| | ° C. | Hrs. | Hrs. | Lbs. | | P. ct. | P. ct. | P. ct. | | Hrs. | P. ct. | P. ct. | P. ct. | P. ct. | Parts. | Parts. | Parts. | Parts. | Lbs. | Points. | Points. | Points. | Mtrs. | P. ct. | |
| 99 | 133 | 2 | 3 | 74.2 | 63 | 4.98 | 4.74 | .30 | 19.7 | 4.72 | 60.40 | (2) | (2) | | | | | | | | | | | | |
| 98 | 133 | 2 | 3 | 74.2 | 63 | 4.99 | 4.49 | .50 | 8.99 | 4.92 | [1] 55.20 | | | | 44 | 33 | 28 | 195 | | | | | | | |
| 75 | 135 | 2 | 3 | 74.2 | 63 | 5.02 | 4.40 | .62 | 7.1 | 5.25 | 46.21 | 3.05 | 43.16 | 50 | 58 | 45 | 40 | 157 | 54.0 | 43.0 | 0.80 | 1.03 | 6,975 | 2.31 | 180 |
| 67 | 135 | 2 | 3 | 74.2 | 63 | 5.02 | 4.35 | .67 | 6.49 | 5.33 | 46.29 | 2.17 | 44.12 | 40 | 66 | 54 | 48 | 132 | 43.5 | 37.5 | .86 | 1.08 | 7,350 | 1.86 | 277 |
| 74 | 135 | 2 | 3 | 74.2 | 63 | 5.01 | 4.20 | .81 | 5.18 | 5.50 | 45.33 | 1.45 | 43.88 | 20 | 66 | 55 | 51 | 128 | 44.5 | 37.0 | .83 | 1.02 | 7,975 | 2.12 | 147 |
| 72 | 135 | 2 | 3 | 74.2 | 63 | 5.06 | 4.04 | 1.02 | 3.96 | 6.50 | 45.03 | .98 | 44.05 | 13 | 72 | 64 | 59 | 105 | 51.0 | 46.4 | .91 | 1.16 | 7,500 | 2.22 | 262 |
| 79 | 135 | 2 | 3 | 74.2 | 63 | 5.00 | 3.72 | 1.28 | 2.90 | 6.95 | 45.07 | .80 | 44.27 | 12 | 72 | 66 | 61 | 101 | 43.5 | 36.9 | .85 | 1.10 | 7,345 | 3.00 | 421 |
| 70 | 135 | 2 | 3 | 74.2 | 63 | 5.06 | 3.53 | 1.53 | 2.31 | 7.07 | 45.37 | .75 | 44.62 | 12 | 75 | 66 | 64 | 95 | 45.0 | 40.8 | .91 | 1.25 | 7,838 | 2.32 | 356 |
| 71 | 135 | 2 | 3 | 74.2 | 63 | 5.04 | 2.95 | 2.09 | 1.41 | 7.75 | 45.80 | .81 | 44.99 | 12 | 73 | 66 | 62 | 99 | 42.5 | 37.6 | .88 | 1.14 | 8,030 | 2.25 | 282 |
| VARYING TOTAL $SO_2$. | | | | | | | | | | | | | | | | | | | | | | | | | |
| 81[3] | 135 | 2 | 3 | 74.2 | 63 | 6.98 | 5.59 | 1.39 | 4.01 | 6.00 | 45.32 | 1.01 | 44.31 | 10 | 74 | 67 | 63 | 96 | 39.5 | 34.3 | 0.84 | 1.05 | 7,115 | 2.71 | 319 |
| 86 | 135 | 2 | 3 | 74.2 | 63 | 6.00 | 4.80 | 1.20 | 4.00 | 6.35 | 45.06 | 1.04 | 44.02 | 14 | 71 | 64 | 60 | 105 | 41.5 | 32.1 | .77 | 1.01 | 6,135 | 2.97 | 247 |
| 87 | 135 | 2 | 3 | 74.2 | 63 | 5.04 | 4.03 | 1.01 | 3.99 | 6.73 | 45.17 | .96 | 44.21 | 14 | 74 | 65 | 61 | 100 | 46.5 | 37.5 | .81 | 1.05 | 5,895 | 2.85 | 376 |
| 88 | 135 | 2 | 3 | 74.2 | 63 | 3.99 | 3.19 | .80 | 3.99 | 7.08 | 46.67 | 1.37 | 45.30 | 18 | 67 | 57 | 54 | 122 | 44.5 | 34.3 | .77 | 1.01 | 6,195 | 2.56 | 424 |
| 89 | 135 | 2 | 3 | 74.2 | 63 | 3.02 | 2.41 | .61 | 3.95 | 7.42 | 47.45 | 3.80 | 43.65 | 45 | 60 | 48 | 41 | 151 | 50.0 | 42.1 | .84 | 1.09 | 6,245 | 2.68 | 466 |
| VARYING TEMPERATURE. | | | | | | | | | | | | | | | | | | | | | | | | | |
| 90 | 148 | 2 | 3 | 74.2 | 63 | 5.03 | 4.03 | 1.00 | 4.03 | 5.02 | 45.42 | 1.84 | 43.58 | 22 | 67 | 56 | 52 | 125 | 43.5 | 29.1 | 0.67 | 0.88 | 5,510 | 2.69 | 163 |
| 91 | 140 | 2 | 3 | 74.2 | 63 | 5.02 | 4.02 | 1.00 | 4.02 | 6.00 | 45.70 | 1.32 | 44.38 | 19 | 68 | 57 | 53 | 122 | 45.5 | 38.2 | .84 | 1.08 | 5,965 | 3.12 | 733 |
| 92 | 130 | 2 | 3 | 74.2 | 63 | 5.04 | 4.02 | 1.02 | 3.94 | 8.17 | 46.15 | 1.24 | 44.91 | 14 | 72 | 61 | 55 | 112 | 53.0 | 47.5 | .90 | 1.21 | 6,480 | 3.20 | 1,077 |
| 94 | 120 | 2 | 3 | 74.2 | 63 | 5.03 | 4.02 | 1.01 | 3.98 | 11.97 | 46.59 | 1.15 | 45.44 | 12 | 69 | 60 | 56 | 115 | 51.0 | 46.0 | .90 | 1.22 | 6,390 | 3.39 | 1,174 |
| 97 | 115 | 2 | 3 | 74.2 | 63 | 5.04 | 4.03 | 1.01 | 3.99 | 14.72 | 47.10 | .88 | 46.22 | 13 | 66 | 56 | 51 | 127 | 52.0 | 50.8 | .98 | 1.28 | 6,430 | 4.00 | 1,565 |
| 100 | 110 | 2 | 3 | 74.2 | 63 | 5.03 | 4.02 | 1.01 | 3.98 | 24.75 | 49.00 | .67 | 48.33 | 11 | 64 | 55 | 49 | 132 | 43.0 | 39.0 | .91 | 1.22 | 6,645 | 3.33 | 995 |

[1] Pulp from this cook was given severe beater treatment to open up the chips present. [2] Pulp discarded. [3] Bad leak developed in third hour of this cook.

## EFFECT OF VARYING TOTAL SULPHUR DIOXIDE.

Cooks were made varying the amount of total $SO_2$ from 3.02 to 6.98 per cent, but in each case the ratio of free to combined $SO_2$ was kept at 4 to 1 and the temperature at 135° C. Figure 9 gives the curves

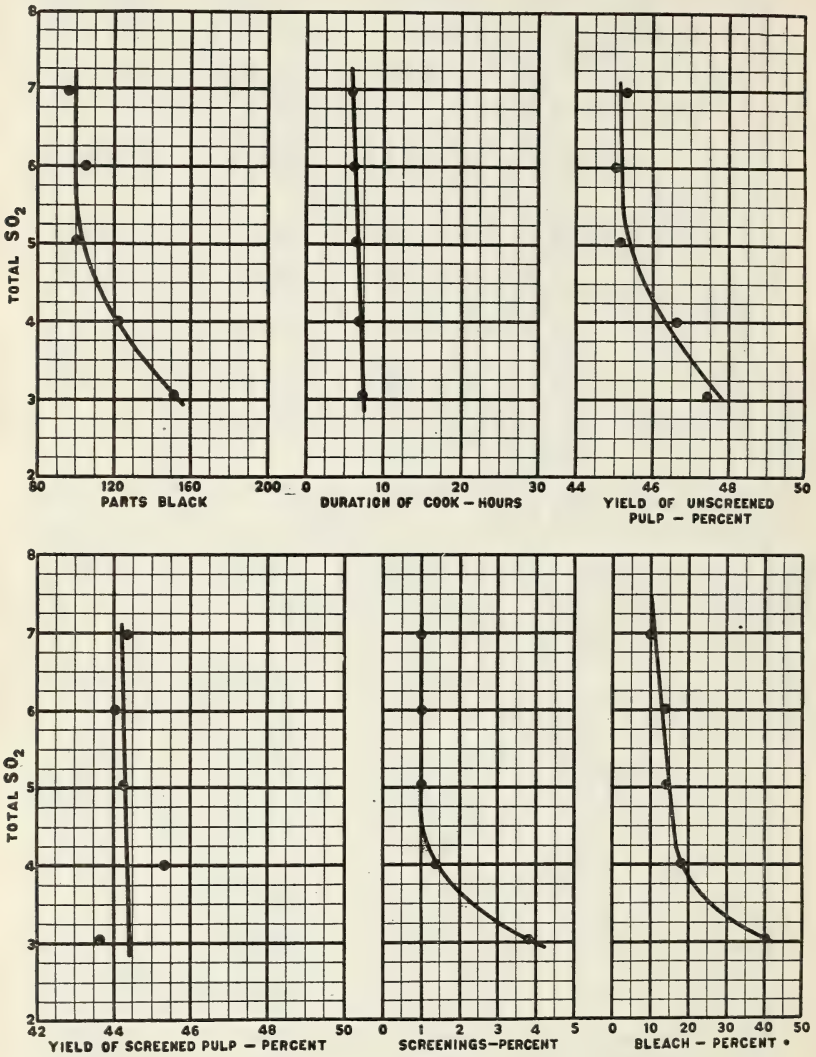



FIG. 9.—Effect of varying the amount of total $SO_2$ in the cooking liquor.

showing the effect on the different factors studied, parts black, duration of cook, yields, and bleach consumed. While these cooks were made with the ratio of free to combined $SO_2$ of 4 to 1, the actual amount of combined sulphur dioxide in the cooking liquor decreased with the total, as shown in Table 3.

The curve for parts black shows that after a total of 5 per cent is reached, any increase in the total $SO_2$ does not produce a lighter pulp, but below that point there is a rapid darkening. An increase in the total $SO_2$ causes a shortening in the cooking time, as would be expected. The yield of unscreened pulp and screenings shows a decrease as the total $SO_2$ is increased, which becomes only slight as a total $SO_2$ of 5 per cent is reached. The yield of screened pulp remains practically constant, because even if the amount of unscreened pulp is increased as the total $SO_2$ is decreased, the amount of screenings increases in almost the same amount. An increase in the total $SO_2$ causes a decrease in the amount of bleaching powder necessary to bleach the pulp to a standard white. Below 4 per cent there is a rapid increase, while above that point there is a gradual decrease in the bleaching powder necessary. The strength tests in this series as in the previous one, were unfortunately very irregular and no conclusions could be arrived at from them.

A study of the curves shows that below 5 per cent total $SO_2$ there is a decided effect on some of the factors studied. At 5 per cent total $SO_2$ the liquor had a combined $SO_2$ of 1.01 per cent; and at the 4 and 5 per cent total $SO_2$, a combined $SO_2$ of 0.80 and 0.61 per cent, showing again that as we go below 1 per cent in combined sulphur dioxide, the parts black, the amount of screenings, and the bleach consumed rapidly increase, for the reason that there is less cooking action.

Photomicrographs of the pulps obtained in cooks 81, 86, 87, and 89 are shown on Plates V, VI, VII, and VIII. Cook 81, which was made with a high total $SO_2$, is more thoroughly cooked than cook 89, which was made with a low total. The latter contains much lignified fiber, the result of having the low percentage of lime in the liquor.

### EFFECT OF VARYING THE TEMPERATURE OF COOKING.

To study the effect of variations in temperature, cooks were made using an acid of the same composition in each case, but varying the temperature from 110° to 146° C. Figure 10 shows the effect on parts black or color of the pulp, on duration of cook, on yields of pulp and screenings, and on amount of bleaching powder necessary to bleach the pulp to a standard white.

Varying the temperature has little or no effect on the color of pulp produced. The duration of cooking rapidly increases as the temperature is lowered, and apparently there would be very little cooking action under 110° C. At 146° C. the cook finished in a little over 5 hours, while at 110° it took almost 25 hours. The yields of screended and unscreened pulp both increase as the temperature is lowered, especially between 120° and 110°, where there is an increase of almost 3 per cent. In the other 10-degree periods the increase amounts to

only about 0.5 per cent. This probably is due to a decrease in the amount of hydrolysis of the cellulose occurring under 120° C. The screenings decreased with the temperature. The explanation for this is that with the higher temperature the cooks are finished before the

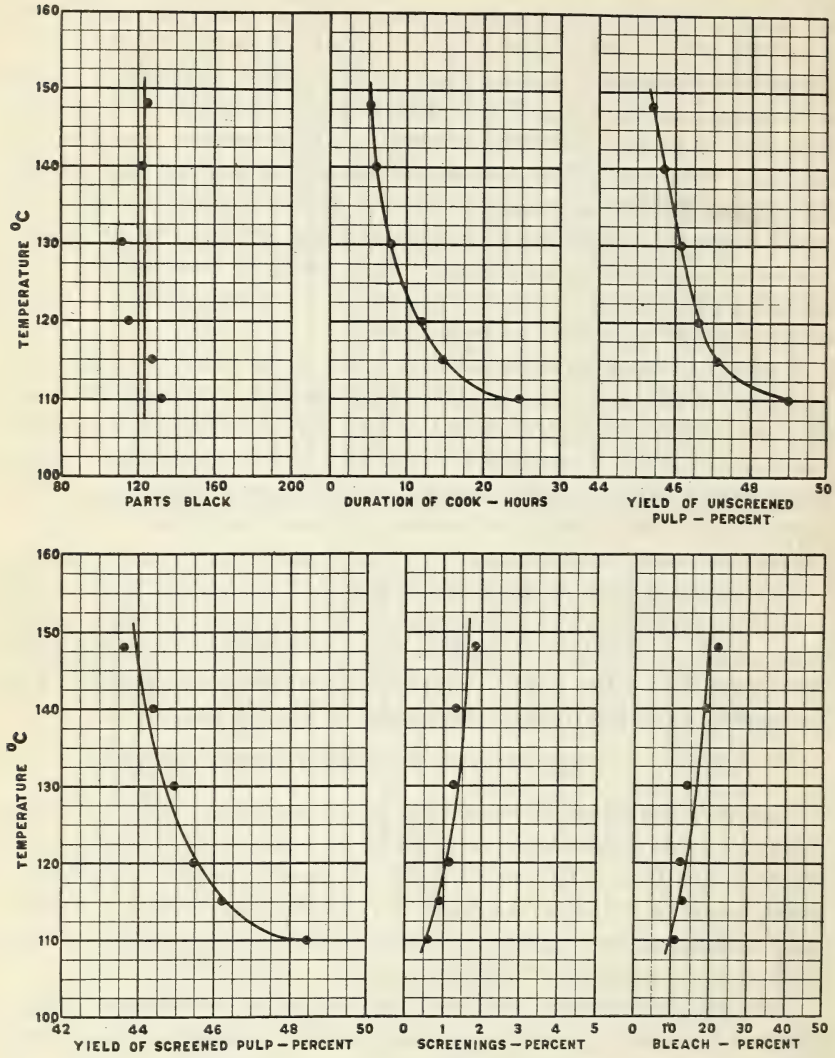
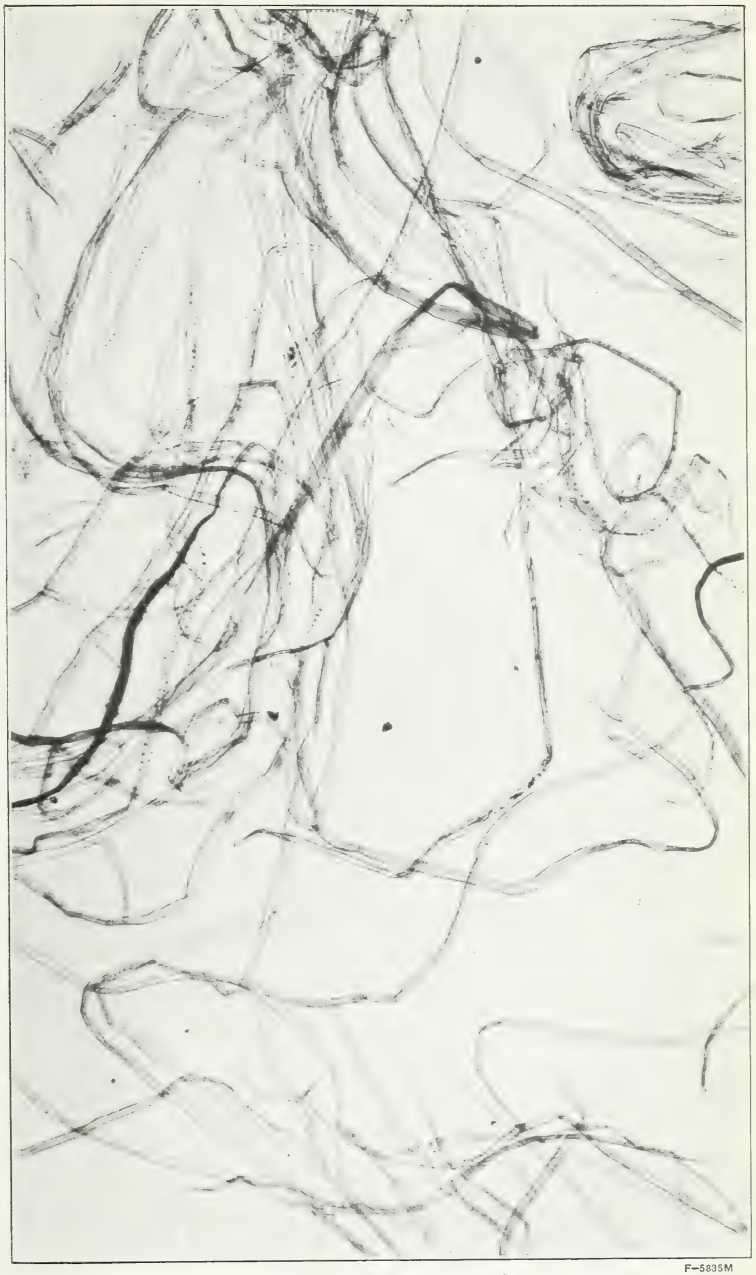


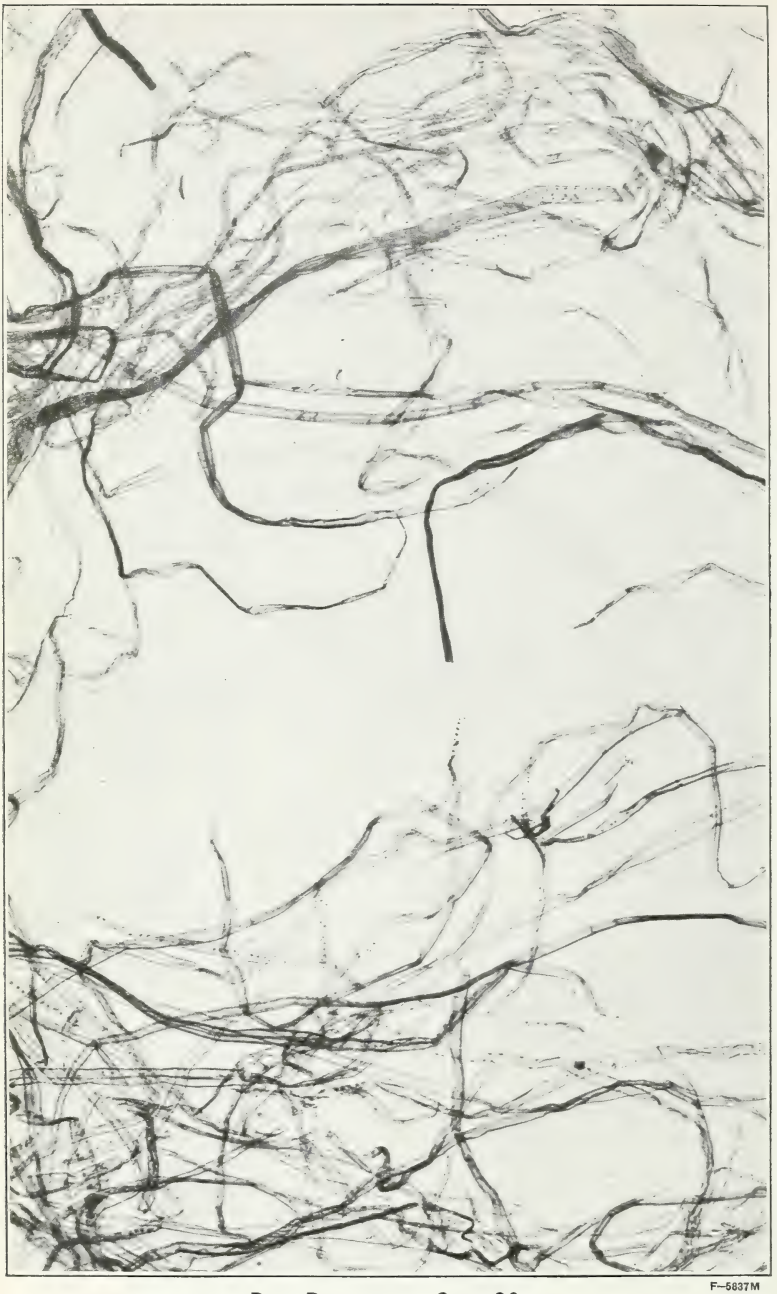

FIG. 10.—Effect of varying the temperature of cooking.

inner portions of some of the larger chips are thoroughly cooked, while the smaller ones are probably overcooked. The lower temperatures with their longer cooks insure a more even cooking and therefore produce less screenings. Decrease in the temperature produced a



F–5835M

PULP PRODUCED IN COOK 81.

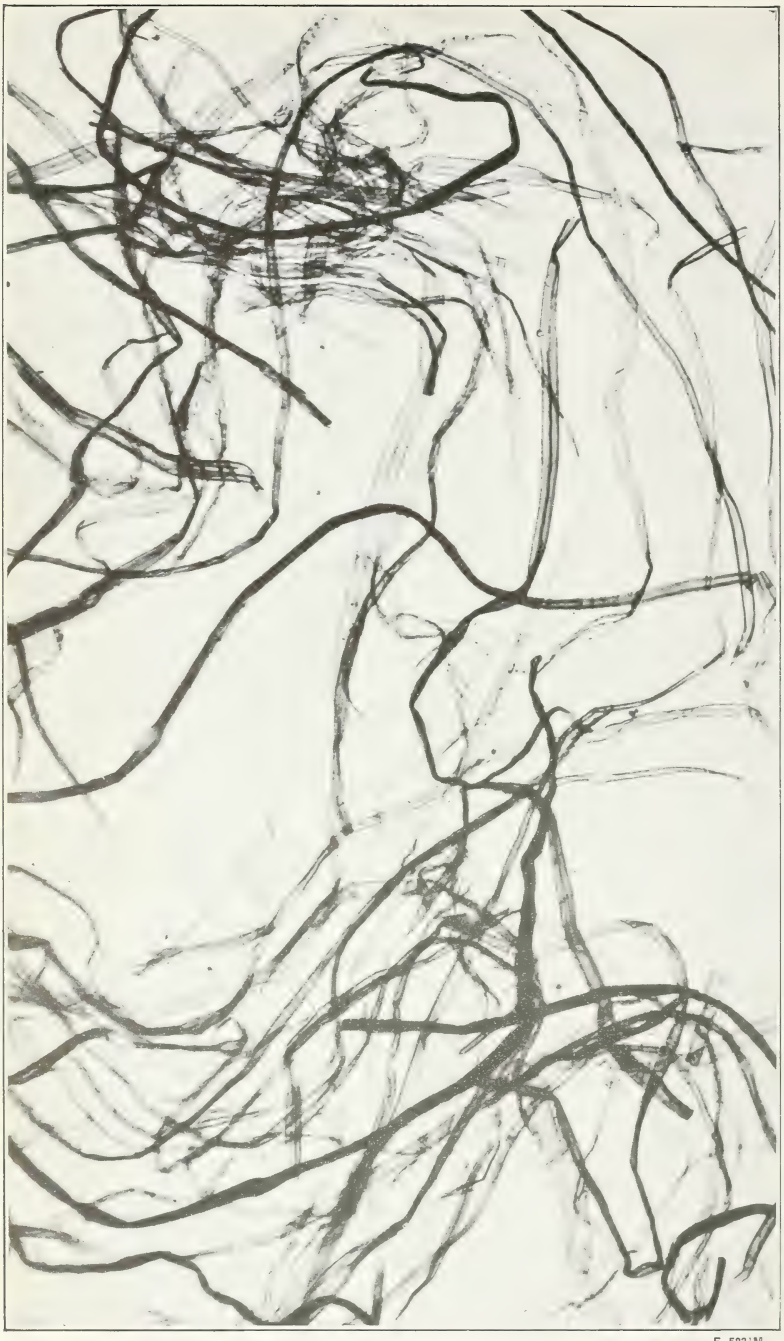


F–5837M

PULP PRODUCED IN COOK 86.

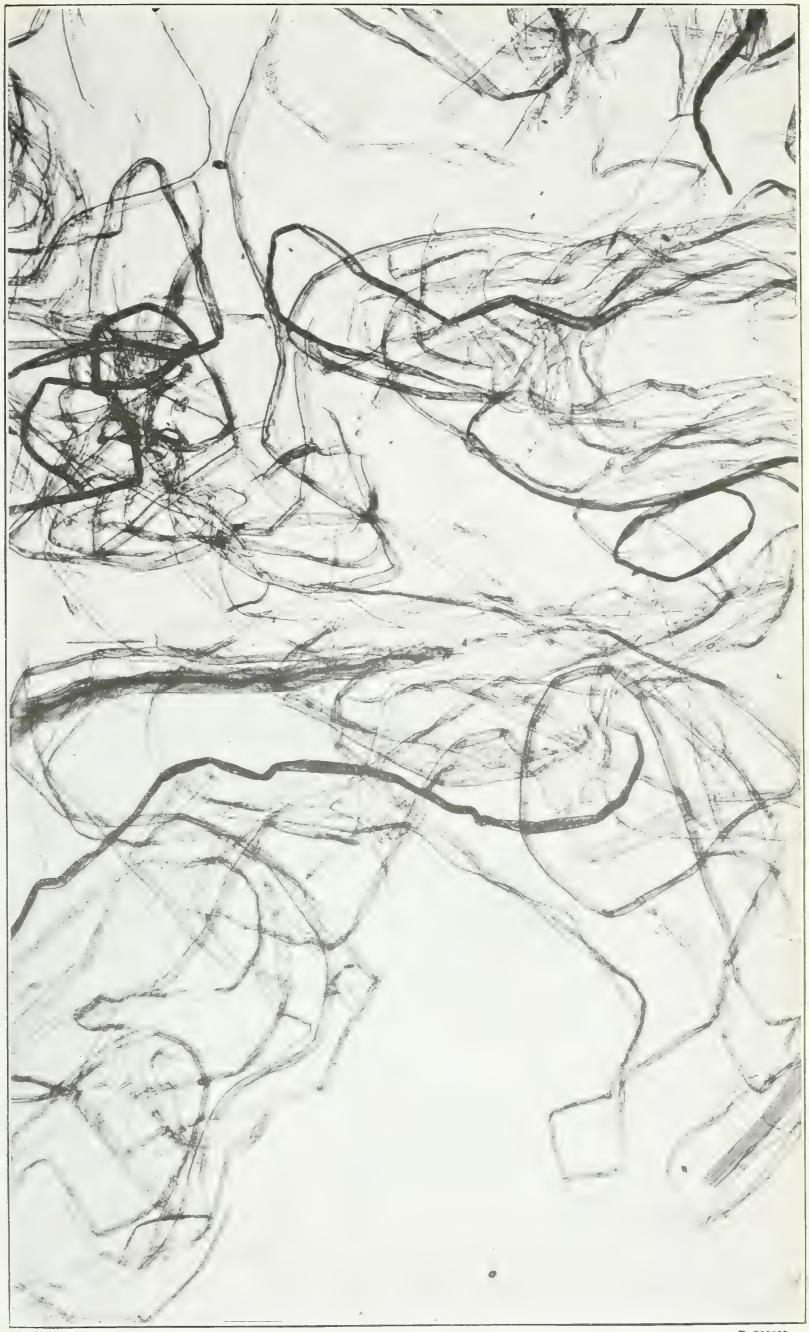
F—5838M

PULP PRODUCED IN COOK 87.



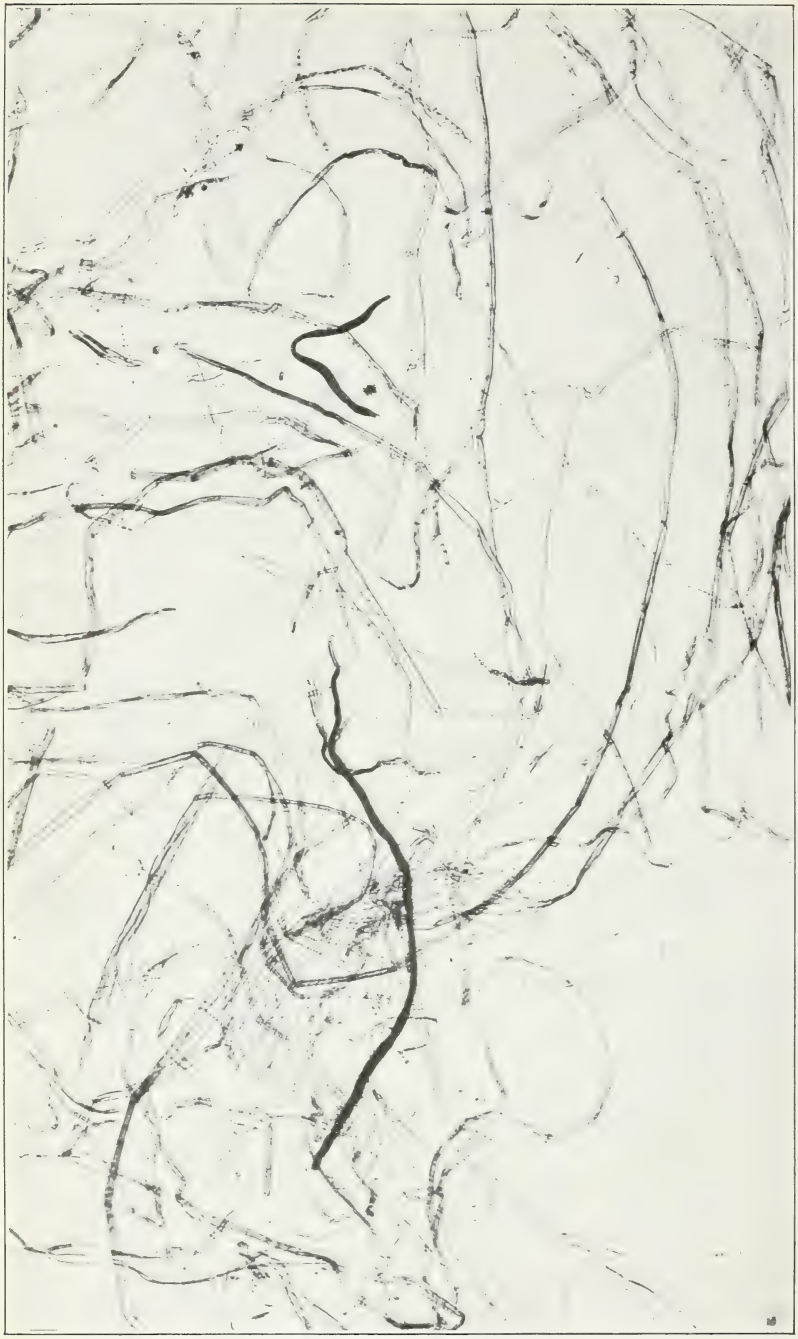
F–5831M

PULP PRODUCED IN COOK 89.



F–5832M

PULP PRODUCED IN COOK 90.

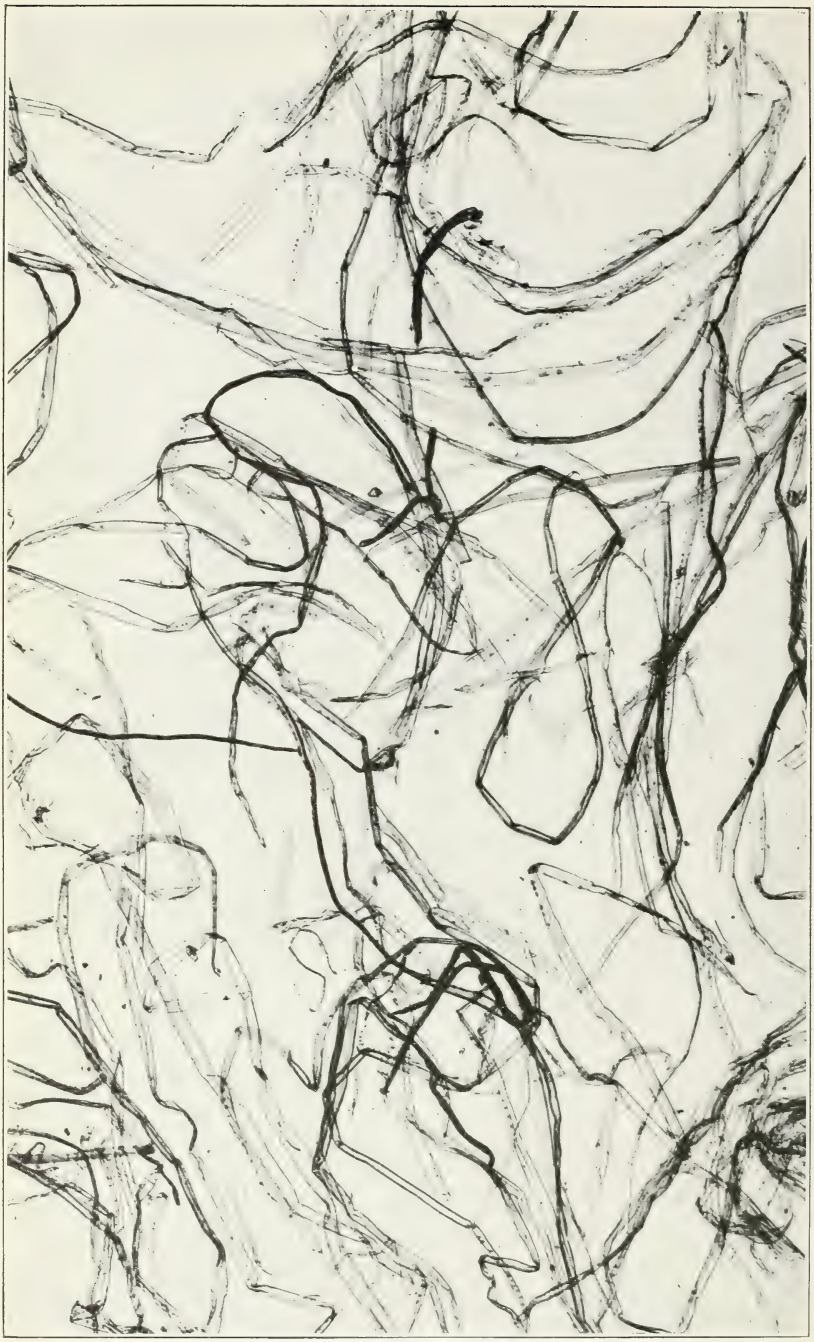


F–5842M

PULP PRODUCED IN COOK 92.

F–5830M

PULP PRODUCED IN COOK 97.



F-5836M

PULP PRODUCED IN COOK 100.

decrease in the amount of bleach consumed, as indicated by the curve. This is rather surprising when one considers that the yield of screened pulp increased almost 5 per cent, while the bleach decreased from 22 to 11 per cent. This must be due to the more uniform cooking occurring at the lower temperatures so that broken up, uncooked shives did not consume bleach. The values for strength are fairly regular (Table 3), probably as a result of the use of an improved style of beater in this series. As would be expected, they show an increase in strength with decrease in temperature.

Photomicrographs of the pulps produced in cooks 90, 92, 97, and 100 are shown on Plates IX, X, XI, and XII. Cook 90, which was made with a high temperature, contains much lignified fiber and is not very uniform; while cook 100, which was made at a low temperature, seems to be well cooked and has fibers nearly all of the same length.

## SUMMARY OF RESULTS.

1. These experiments have demonstrated that a standard color can be used with which to match the color of the liquor in the digester to determine when a cook is finished. A cook can be duplicated at any time by comparison with this standard.

2. The limit to which the combined $SO_2$ can be decreased to obtain good cooking seems to be about 1 per cent. Below this there is a rapid darkening of the pulp produced, and an increase in the screenings and bleach consumed.

3. When the temperature and total $SO_2$ are kept constant, the yield of screened pulp increases somewhat with increase in the combined $SO_2$, because of the more thorough cooking. Consequently, less screenings are obtained.

4. When the temperature and total $SO_2$ are kept constant, a decrease in the amount of combined $SO_2$ causes quicker cooking action, so that a cook can be finished in less time.

5. An increase in the total $SO_2$ causes a decrease in the cooking period, other factors remaining constant.

6. The screenings and color of the pulp remain constant as the total $SO_2$ is decreased to about 5 per cent, after which there is a rapid increase in both of these factors.

7. The higher the total $SO_2$, the easier it is to bleach the pulp, other factors being the same.

8. The amount of screenings decreases as the temperature is lowered, because of the more even cooking obtained at the lower temperatures.

9. The bleach is reduced as the temperature is decreased, while the yield of pulp increases.

## METHODS OF ANALYSIS AND OTHER TESTS.

### BONE-DRY WEIGHT.

The bone-dry weight was determined by taking a sample of the wood, pulp, or screenings and drying to constant weight in an oven at 104° C. The ratio of the weight after drying to that before drying then became the factor by which the bone-dry weight of the entire amount was calculated. All yields and similar calculations are made on the basis of bone-dry weight.

### COLOR.

The color of the pulp was determined by means of the Ives tint photometer. By means of this apparatus the color of the paper is reduced into parts of the three primary colors, red, green, and blue. When these three add up to 300, as in the case of the magnesia standard used for comparison, then pure white is obtained. The sum of the three primary colors subtracted from 300 gives the "parts black" of the paper in question and is a measure of its color, the higher the parts black, the darker the pulp.

### BLEACH REQUIRED.

The bleaching solution was made by mixing bleaching powder with water, allowing the sediment to settle and drawing off the clear solution. Its strength was determined by titrating 10 cc with $\frac{0.987N}{10}$ solution of sodium arsenite using starch iodide paper as an outside indicator. The number of cubic centimeters necessary to complete the titration gives the gram per liter of 35 per cent bleach. Twenty-five grams (bone-dry) of the pulp were put in enameled jars with 2,000 cc of water and thoroughly mixed. The calculated amount of bleach liquor was then added and jars placed in a water bath heated with an electric coil which kept it a temperature of 110° F. The contents of the jar were kept in motion by means of a stirring apparatus until all the bleach was exhausted. The pulp was then thoroughly washed, made into hand sheets, and its color compared with a standard to which the addition of more bleach would not make it any whiter. The per cent of bleach necessary to give a standard white is expressed in per cent of the bone-dry weight of the pulp.

## ANALYSIS OF COOKING LIQUOR.

### PREPARATION OF $\frac{N}{16}$ IODINE.

The iodine solution is made by diluting from a concentrated solution. This was made by dissolving 156.7 grams of iodine and 217 grams of potassium iodide in about 250 cc of water and diluting to 1

liter. Two hundred cc of this solution make 4 liters of approximately $\frac{N}{16}$ iodine. This is then standardized against $\frac{N}{16}$ sodium thiosulphate solution.

### PREPARATION OF $\frac{N}{16}$ SODIUM THIOSULPHATE.

Weigh out 24.7 grams of sodium thiosulphate, dissolve in water, and dilute to 1,000 cc. This is standardized according to any of the standard methods.

### DETERMINATION OF TOTAL $SO_2$.

A 300 cc Erlenmeyer flask is filled with about 150 cc distilled water and enough $\frac{N}{16}$ iodine solution added so that only about 2 cc of the iodine solution will complete the titration. Two cc of the liquor to be analyzed are then added to this and the titration completed, using starch solution as an indicator. This gives the total $SO_2$ present and every cc on the burette reads to one-tenth of 1 per cent.

### DETERMINATION OF FREE $SO_2$.

A 300 cc Erlenmeyer flask is filled with about 150 cc of distilled water and enough $\frac{N}{16}$ sodium hydrate added so that only about 2 cc will complete the titration. Two cc of the liquor to be analyzed are then added and the titration completed using phenolpthalein as an indicator. Each cubic centimeter is equal to one-tenth of 1 per cent of free $SO_2$. The difference between the free and total gives the $SO_2$ present combined with lime, and multiplying the amount of combined $SO_2$ by 0.875 gives the amount of lime (CaO) in combination.

## PUBLICATIONS ON PULP AND PAPER.

Paper Pulp from Various Woods. Forest Service Bulletin (unnumbered), by Henry E. Surface. (Out of print.)

Experiments with Jack Pine and Hemlock for Mechanical Pulp. Forest Service Bulletin (unnumbered), by J. H. Thickens. (Out of print.)

*Bibliography of the Pulp and Paper Industries. Forest Service Bulletin 123, by Henry E. Surface. Price 10 cents.

*The Grinding of Spruce for Mechanical Pulp. Forest Service Bulletin 127, by J. H. Thickens. Price 15 cents.

*Suitability of Longleaf Pine for Paper Pulp. Department of Agriculture Bulletin 72, by Henry E. Surface and Robert E. Cooper. Price 5 cents.

*Effects of Varying Certain Cooking Conditions in Producing Soda Pulp from Aspen. Department of Agriculture, Bulletin 80, by Henry E. Surface. Price 15 cents.

*Ground Wood Pulp. Part I, Grinding of Cooked and Uncooked Spruce; Part 2, Substitutes for Spruce in the Manufacture of Ground Wood Pulp. Department of Agriculture Bulletin 343, by J. H. Thickens and G. C. McNaughton. Price 5[0]t cents.

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